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## PATENT SPECIFICATION

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(72) Inventors ROBERT LECLERCO PHILEAS CAPOUILLET and ALBERT VAN CAUTER



## (54) COATING OF GLASS

We, BFG GLASSGROUP, a Groupement d'Interet Economique, established under the laws of France (French Ordinance dated 23rd September 1967), of Rue Caumartin 43, 75009 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for forming a metal or metal compound coating on a face of a glass substrate by contacting such face while it is at elevated temperature with a gaseous medium consisting of or containing a substance or substances in gaseous phase, which substance(s) undergo(es) chemical reaction or decomposition to form said metal or metal compound on said face. The invention also relates to apparatus for use in carrying out such a process.

Processes of the above kind are employed for forming coatings which modify the apparent colour of the glass and/or which 25 have some other required properties in respect of incident radiation, e.g. an infrared-reflecting property.

The known processes do not always enable coatings with satisfactory properties to be 30 achieved. Difficulties are encountered in forming coatings sufficiently quickly to keep pace with industrial production programmes and/or in forming coatings which are of satisfactory quality e.g. in respect of their uniformity of thickness and their optical propertics.

The subject of the patent application is a coating process which affords important advantages in respect of the reliability with which good quality coatings can be formed and/or of the high coating rates which are

The process according to the invention, which is of the kind above referred to, is characterised in that the gaseous medium is caused to flow along the substrate face to be costed as a substantially turbulence-free layer along a flow passage which is defined in part by the face of the glass and which leads to an exhaust ducting via which residual medium is drawn away from said face.

One factor contributing to the good results realisable by this process is the establishment of a substantially turbulence-free flowing laver of the gaseous medium in contact with the face to be coated. The flow of gaseous medium along the flow passage is considered substantially turbulence-free if it is substantially free of local circulating currents or vortices giving rise to a substantial increase in the flow resistance. In other words, the flow is preferably laminar but undulation of the fluid or minor eddy currents can be tolerated provided that the required coating metal or metal compound is formed substantially only at the boundary layer in contact with the hot substrate surface and is not to any significant extent formed as a precipitate within the fluid stream.

Experiments indicate that as compared with hitherto known processes, the process according to the invention makes it easier to form a coating, e.g. a metal oxide coating, providing a uniform coverage of the substrate surface. The superiority of the new process appears to be particularly evident when attempting to build up coatings rapidly e.g. at a rate of at least 700 A of coating thickness per second. The invention therefore promises to be of special importance when coating glass ribbons, in course of continuous production at high speeds, e.g. speeds in excess of 2 metres per minute and even in excess of 10 metres per minute such as are often attained by the float process.

The avoidance of spurious deposits on the substrate surface are more easily avoided if the flow passage within which the coating is formed is shallow. Preferably the height of the flow passage measured normally to the substrate face is at no point in excess of 4Q nım.

The flow passage may be of uniform height or the passage may increase or decrease in height along its length in the direction in which the gas flow takes place.

It is advantageous for the height of the flow passage to decrease in the direction of gas flow therethrough, at least over an end

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portion of its length leading up to the exhaust ducting. By using a flow passage which tapers in that manner it is easier to avoid bicctionable turbulence within the flowing layer of gas. Preferably the flow passage tapers over at least the greater part of its length. An angle of taper of 10° or less is usually satisfactory.

For achieving the best results it is always desirable for the coating to be formed progressively, on successive incremental portions of the substrate face. The invention can be applied for continuously coating a face of a continuous ribbon of glass and in that case it is of course inevitable that the flow passage will occupy only a portion of the length of the said face and the flow passage and substrate must be relatively displaced as the process proceeds. However even when coating a sheet, it is preferable for the flow passage to occupy only an incremental portion of at least one dimension of the face area

placement of the flow passage and substrate so as to form the coating progressively on

to be coated and to bring about relative dis-

successive portions of the face.

Preferably the aforesaid relative displacement occurs in a direction parallel with the direction in which gas flows along the flow passage. In this case all of the successively coated portions of the face are exposed to the same coating conditions integrated over the length of the flow passage. However in some cases good results can be obtained by bringing about such relative displacement in a direction normal to the said gas flow direction along the substrate. For example for coating a sheet the flow passage may extend along one dimension of the sheet and extend across only a portion of the other dimension of the sheet and the latter can be displaced parallel with that other dimension.

The advantages of thes process according to the invention are particularly notable when the process is employed for coating the top face of a ribbon of glass which is in continuous movement at a speed of at least 2 metres per minute, parallel with its longitudinal axis and in the direction of the gas flow through the aforesaid gas flow passage. The flow passage can be quite short, which is an important consideration in view of the limited space which is available in many plants for the production and treatment of continuous glass ribbons. Generally it is preferable for the length of the flow passage (i.e. its dimension measured in the direction of gas flow therethrough) to be not more than 2.0 metres. The length of the flow passage is however preferably in all cases not less than 10 cm.

The invention has been made primarily with a view to the formation of good quality metal oxide coatings on glass substrates. However the invention can be applied for forming coatings of other metal compounds e.g. for

forming a coating of a metallic boride, sulphide, nitride, carbide or arsenide by reacting a corresponding metallic or organometallic compound with a halogenated boron compound, H2S, NH2, CH4, or an arsenic containing compound, in the absence of oxygen. The invention can also be applied for forming a metal coating. For example a coating of nickel can be formed by decomposing nickel carbonyl under the action of heat provided by the heated substrate, in a reducing atmosphere or at least in the absence of oxygen.

For forming a metal oxide coating, the invention includes processes wherein a stream of oxygen or oxygen-containing gas and a separate stream of a vaporised metal compound with which oxygen reacts to form a metal oxide coating on the substrate face are caused to flow continuously into said flow passage. A particular and important embediment of the invention performed in that way employs a stream of a vapourised tin compound and a stream or streams of oxygencontaining gas for forming a tin oxide coat-

However various other metal oxide coatings can be formed in that manner, e.g. a coating of titanium dioxide by reacting titanium tetrachloride with oxygen. The vapourised metal compound will usually be diluted with an inert gas, e.g. nitrogen and the vapour stream may contain additional ingredients for modifying the properties of the coating. For example the vapour stream may contain antimony pentachloride for forming antimony dioxide together with the principal oxide ingredient of the coating.

In certain processes as above referred to for forming a metal oxide coating, a gas stream consisting of or containing a said vapourised metal compound is continuously discharged into the aforesaid flow passage and induces a flow of air into and along such

In some cases the gaseous medium entering the flow passage comprises a layer of vapourised metal compound and a layer of oxidising gas which flows between said layer of vapourised metal compound and the substrate face being coated. When proceeding in that way, the flow of oxidising gas, e.g. air, beneath the layer of vapourised metal compound, promotes rapid formation of the coating so that it commences to form on the substrate at or near the entry end of the flow passage.

In an alternative procedure, the gaseous medium entering the flow passage comprises an upper layer of oxidising gas and a layer of vapourised metal compound which flows beneath such upper layer. The vapourised metal compound may enter the passage in contact with the face of the substrate in which case the upper layer of oxidising gas 130

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tends to prevent the stream of vapourised the ribbon but for the best results it is premetal compound from flowing upwardly away ferable for the mean angle of such discharging from the face of the substrate. A particularly streams with respect to the ribbon to be less advantageous feed system is one wherein a than 45°. In certain embodiments of the invention, the gaseous medium flowing along 70 stream of vapourised metal compound enters the flow passage between overlying and underthe flow passage derives from gas feed streams lying streams of oxidising gas. The result of different compositions which enter the is that the stream of vapourised metal compassage from paths which are at an angle pound is depressed away from the top surface of 20-35° to each other. 75 of the flow passage, so avoiding or reducing The discharge of gas streams into the flow 75 tendency for oxide deposition to occur on passage at an inclination to the substrate as such surface, while at the same time a rapid above described is a feature which can be formation of the metal oxide coating on the adopted with advantage when coating an inglass substrate is promoted by the lower dividual glass sheet or a part thereof. Howstream of oxidising gas. ever, depending on circumstances in a given 80 80 As has already been indicated, it is an industrial plant, there will usually not be such advantage of the invention that good quality a restricted choice of positions for the gas coatings can be formed very rapidly. This feed conduits as there is in a flat glass formpotential advantage is realised in embodiing apparatus. When coating an individual ments of the process wherein the composition 85 sheet, one or more gas streams can be dis-85 of the gaseous medium flowing through the charged into the flow passage parallel with flow passage and the temperature conditions the sheet if so required. to which such medium is exposed are such Preferably the exhaust ducting is in the that the coating forms on the substrate face form of a chimney extending upwardly away at a rate of at least 700 A per second. The 90 from the substrate face being coated. The 90 process as thus performed can be applied for manner in which the flow takes place along forming optical coatings on a fast moving the flow passage is influenced by the suction glass ribbon, e.g. a ribbon advancing through forces which exist at the exit of such flow the coating zone at a speed of 2 metres per passage. The use of a chimney extending up-95 minute or more e.g. greater than 10 metres wardly away from the face has been found to 95 per minute such as is often attained in the be very beneficial for the quality of the coatfloat process. ing. Other arrangements of the exhaust duct-The invention includes a process for coating are however possible. For example the ing a continuous ribbon of glass which is in ducting may be arranged so that gases reach-100 movement parallel with its longitudinal axis ing the exit end of the flow passage are drawn 100 and in the same direction as the direction of off laterally through one or more transverse gas flow along said flow passage, characterducts. This is feasible particularly if the ised in that the gaseous medium flowing along entry end portion of the ducting is subsaid flow passage derives at least in part divided into a series of side by side passage-40 from a gas stream which enters said passage 10 105 ways as hereafter referred to. from a path which is at an angie of 45° or Advantageously, an exhaust ducting is used less to said face. Such a process can be percomprising a plurality of separate passageformed quite conveniently in many existing ways distributed in side by side relationship flat glass production plants because a conacross substantially the whole width of the 110 duit or conduits for delivering the gas can gas flow path through the flow passage. The 110 be installed with little or no modification of exhaust of gas via different exhaust ducting the plant lay-out. The delivery of the or a passageways or through different groups of gas stream at an angle of 45° or less to the passageways may be independently controlled face to be coated is moreover conducive to e.g. by means of independently controllable 115 the formation of a coating of relatively homoextractors, for achieving a required volume 115 geneous or uniform structure, e.g. a structure featuring a regular arrangement of crystals. flow rate profile across the width of the flow passage. The discharge of gases into the flow Particular importance is attached to the passage at an acute angle to the ribbon is performance of a process according to the in-120 favourable also for promoting the required 120 vention for coating a ribbon of glass pronon-turbulent flow of gaseous medium along gressing from a float tank and in that field of the flow passage. If a process according to the application preference is given to processes invention is carried out so that the gaseous in which the flow passage is located downmedium flowing along such passage derives stream of the exit end of the float tank and at 125 from two or more gas feed streams separately a zone where the glass has a temperature in 125 discharged into said passage one above anthe range 100° to 650°C. other, a nicely controlled flow of the medium The invention includes apparatus suitable along the passage can be achieved even if for use in carrying out a coating process one or more but not all of such feed streams according to the invention as hereinbefore

discharge(s) at an angle of less than 45° to

defined. Apparatus according to the invention 130

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by partitions such as 18 into a plurality of exhaust passageways distributed in side by side relationship across substantially the whole width of the gas exhaust path. A vapour mixture containing SnCl, and

SbCl<sub>3</sub> was generated from a liquid phase containing such ingredients in a volume ratio of 100:1 and this vapour mixture, entrained in a stream of nitrogen, was delivered from vessel 11 through the feed channel 12.

The temperature of the glass ribbon at the region beneath the entry end of the flow passage 13 was about 585°C.

The rate of delivery of the vapour mixture into the flow passage 13 and the draught forces through the chimney 15 were regulated so as to establish along said passage a substantially turbulence-free flow of vapour mixed with air induced into the passage by the discharge of the vapour stream, as suggested by the arrows beneath the feed channel 12. Such regulation was moreover such that a coating composed essentially of SnO. together with a small quantity of Sb<sub>2</sub>O<sub>5</sub> serving as doping agent, and having a thickness of 2,500 Å, was formed on the travelling glass ribbon. Regulation of the draught forces can be achieved e.g. by using a regulatable fan in the chinney 15.

The coating on the glass had a green tint viewed by reflected light. The coated glass had a very high visible light transparency but reflected a significant proportion of incident radiation in the far infrared spectral region.

The emissivity of the coating was 0.4; its diffuse luminous transmission was practically

Examination of the coating showed that it had an homogeneous structure and had uniform thickness and optical properties.

A coating method as above described can be performed in the same way for coating a continuous ribbon of sheet glass traveiling from the drawing chamber of a Libbey-Owens type drawing machine. For example the compartment 4 can equally well be regarded as located within the annealing gallery adjoining such drawing machine.

Example 2

A coating process was performed in the same way as Example 1 but the vapour mixture forming the coating composition derived from a solution of stammous acetate and a small proportion of SbCl3 in glacial acetic acid, the SbCl<sub>3</sub> being added as doping

The vapour mixture from this solution was entrained into contact with the glass ribbon in a stream of nitrogen from which all traces of oxygen had been removed. The glass ribbon had a temperature of about 585°C at the place of initial contact by the vapour mixture. The glass ribbon speed was 6 metres per minute.

A coating of SnO2 together with a small quantity of antimony oxide and having a thickness of 4000 A, was formed on the glass ribbon. The delivery rate of the vapours along feed channel 12 and the draught forces through the chimney 15 were regulated so that the vapours were maintained in substantially turbulence-free flow along flow passage 13 and the coating oxides were formed substantially only at the boundary layer of vapour in contact with the hot glass ribbon.

The coating had a greenish tint, viewed by reflected light. The coating had a high transparency to light in the long wavelength region of the visible spectrum and reflected a significant proportion of incident radiation in the far infrared wavelength band.

The emissivity of the layer was 0.3. The diffuse luminous transmission of the coating was practically nil.

The thickness of the layer and its optical properties appeared to be truly uniform and its structure was homogeneous over the whole area of the coating.

In another process according to the invention, coatings of good quality were formed by following a procedure as just described but using as the feed stock vapours of ZrCl, entrained in a stream of dry air. A layer of ZrO2 was formed having a grey tint viewed by reflected and by transmitted light.

Example 3

Using a coating apparatus as represented in Figs. 1 and 2 and described in Example 1, vapours of titanium isopropylate

 $(Ti(OC_3H_*)_*$ 

entrained in a current of nitrogen were delivered through the feed channel 12, to contact a glass ribbon where its temperature was about 605°C. The ribbon speed was 7 metres per minute.

The rate of delivery of the vapour mixture and the aspiration of gases from the flow passage 13 into the chimney 8 were regulated so as to establish a substantially non-turbulent vapour flow along passage 13 and so that a coating layer of TiO, having a thickness of 550 A was formed on the glass ribbon.

The coating appeared white by reflected light. The refractive index of the coating was 115 2.49. The diffuse luminous transmission of the coated glass was practically nil.

Examination of the coating showed that its thickness, structure and optical properties were substantially uniform.

Example 4

Coating apparatus as represented in Fig. 3 was used for coating a glass ribbon 19 during its conveyance on rollers 20 through a compartment 21 of a gallery having refractory 125

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roof and sole walls 22, 23. The compartment 21 has end walls formed by displaceable refractory screens 24, 25. The coating apparatus comprises a shroud 26 defining with the top face of the longitudinally moving glass ribbon 19 a shallow gas flow passage having a length of 40 cm and a uniform height of 15 mm extending over substantially the full width of the glass ribbon. Twin feed channels 27 and 28 lead from gas reservoirs 29 and 30 respectively into the entry end of the horizontal flow passage beneath the shroud 26. The feed channel 27 is inclined at an angle of 30° to the glass ribbon whereas the angle of inclination of the feed channel 28 is 50° At its exit end the horizontal flow passage is subdivided by vanes such as 31 into a plurality of side by side exit portions which lead into exhaust ducting 32. This ducting comprises two horizontal exhaust tubes disposed at right angles to the longitudinal axis of the shroud 26 and leading in opposite directions therefrom. Each of such tubes was provided with an extractor fan (not shown). A ribbon of glass was conveyed through the coating station at a speed of 17 metres per minute. The temperature of the glass at the coating station was 580°C. Vapours of iron acetylacetonate entrained in a current of dry nitrogen were fed along feed channel 27. A current of oxygen was delivered along feed channel 28. The rate of feed of the gases through the feed channels 27 and 28 and the aspirating forces acting via the exhaust ducting were regulated in such manner that the mixture of gases deriving from feed channels 27 and 28 was maintained in substantially

turbulence free flow along the flow passage

beneath shroud 26 and a coating of Fe<sub>2</sub>O<sub>3</sub> having a thickness of about 500 A was

formed on the glass ribbon. The coating

appeared yellow-amber by transmitted light.

Examination of the coating showed that its

uniform thickness and optical properties. By appropriate choice of the starting materials a coating of cobalt oxide can be formed in a similar manner. By employing a suitable mixture of vapours, coatings having different colourations and comprising a mixture of oxides, e.g., a mixture of oxides in the group Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> can be

structure was homogeneous and that it had

In the above coating method the gallery in which the compartment 21 is located is an annealing gallery connected to a float tank. This coating method could also be performed for coating a ribbon of float glass before admission in the annealing gallery. It could as well be performed for coating a glass ribbon of some other origin, e.g. a ribbon formed in a Libby Owens drawing machine.

Coating apparatus as described with reference to Fig. 3 could be employed in a similar manner for coating individual sheets of glass during their transportation through a coating

station.

formed.

Example 5

By means of apparatus as used as shown in Fig. 3 coatings of various compositions, of uniform thickness and optical properties, and having an homogeneous structure were formed on ribbons of glass in course of their manufacture.

The Table below gives the reactants employed for forming such coatings, also the temperature of the glass on contact thereof by the reactants the composition of the formed coating and certain properties thereof.

In each case dry nitrogen was employed as inert carrier for the reactants, and the coating was effected in an environment free from oxygen. The coated glass was kept out of contact with air until the temperature of the glass was sufficiently low to avoid risk of chemical modification of the coating.

		TABLE					
90	1st Reactant, fed through passage 27	2nd Reactant, fed through passage 28	Glass Temp. °C.	Composition of formed coating	Properties of coating		
	Pb(C,H.),	H <sub>2</sub> S	200	PbS	Grey in reflection, yellow- brown in transmission, for thickness of 500 Å		
95	SiH,	NH <sub>a</sub>	600	Si <sub>3</sub> N <sub>4</sub>	Very chemically stable; re- fractive index near that of glass; thus nearly invisible		
	Cr(CO),	CH,	150	Cr <sub>3</sub> C <sub>2</sub>	Hard; acid resistant; light- reflecting grey-neutral in transmission		
100	$Ga(CH_a)_a$	(CH <sub>2</sub> ):AsCN	250	GaAs	Semi-conductive		

Sheets of glass can be coated under the same conditions.

Example 6 A ribbon of glass was coated using appara-105 tus as represented in Fig. 3. On teaching the coating station the glass ribbon had a temperature of 600°C. The ribbon was exposed at the coating station to an atmosphere free from oxygen and enriched in hydrogen.

Vapours f vanadium chloride (VCI,) entrained in a stream of hydrogen were fed to

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the glass along feed channel 27. Boron bromide vapours (BBr<sub>3</sub>) entrained in a stream of hydrogen were fed through feed channel

At a coating zone within the shroud 26 a coating of vanadium boride (VB<sub>2</sub>) formed on the glass ribbon. The coating appeared grey. The successively coated portions of the ribbon were not brought into contact with air until their temperature had fallen sufficiently to avoid risk of chemical modification of the coating.

Coatings of metallic silicon can be formed in similar manner by exposing the glass while at a temperature of 500°C to vapours of silicon hydride (SiH<sub>4</sub>). In such a process it is essential to protect the coating from oxidation.

Individual sheets of glass can be coated under the same conditions.

Example 7

Sheets of glass were coated in an apparatus as shown in Fig. 4. The glass sheets, one of which is shown and is designated 33, were placed on a conveyor 34 and transported thereby through a coating station. The glass sheets on reaching such station had a temperature of approximately 200°C.

At this coating station there is an enclosure (not shown) through which the conveyor 34 passes and within this encosure there is a gas flow passage 35 through which a gas stream containing the precursor of the coating material is caused to flow in contact with the glass, in a direction transverse to the direction of movement of the glass sheets. A feed channel 36 leads horizontally to such flow passage from an entrance shaft 37. Surplus gases leaving passage 35 escape through exhaust ducting 38 the entry end of which is internally subdivided by partitions 39 into a plurality of side by side flow paths.

The length of the flow passage 35 (i.e. its dimension normal to the direction of movement of the glass sheets) is 1 m and its height is 20 mm.

The aforesaid enclosure at the coating station was kept filled with nitrogen, to the exclusion of oxygen, at slightly above atmospheric pressure in order to avoid inducement of air into the coating zone. Nickel carbonyl vapours, entrained in a stream of nitrogen were delivered through feed channel 36. The rate of delivery of this feed stock and the rate of extraction of surplus gases through the exhaust ducting 38 were such as to establish a substantially turbulence-free flow along the passage 35 and ensure that a coating was formed on the surface of the glass sheets, which coating was formed substantially exclusively by the decomposition of the organic substance at the boundary layer of vapour in contact with the hot glass sheets. The result was that a coating of nickel 100 A in thickness, was formed on each glass sheet. The coatings appeared grey by transmitted and by reflected light. Each coating was of uniform thickness and had uniform structure and optical properties. The coatings uniformly transmitted light over a broad visible wavelength band. The coatings showed minimal diffuse luminous transmission.

By the control of the atmosphere to which the coatings formed on the sheets were exposed at the coating station and by keeping the temperature of the glass sheets on leaving the coating station sufficiently low, modification of the coatings on contact with air was avoided.

WHAT WE CLAIM IS:—

1. A process of forming a metal or metal compound coating on a face of a glass substrate by contacting such face while it is at elevated temperature with a gaseous medium consisting of or containing a substance or substances in gascous phase, which substance(s) undergo(es) chemical reaction or decomposition to form said metal or metal compound on said face, characterised in that said gaseous medium is caused to flow along said face as a substantially turbulence-free layer along a flow passage which is defined in part by the face of the glass and which leads to an exhaust ducting via which residual medium is drawn away from said face.

2. A process according to claim 1, characterised in that the height of said flow passage, measured normally to said face, is at no point in excess of 40 mm.

3. A process according to claim 1 or 2, characterised in that said flow passage tapers in the direction of gas flow therethrough, at least over an end portion of its length leading up to said exhaust ducting.

4. A process according to any preceding claim, characterised in that said flow passage occupies only an incremental portion of at least one dimension of the area to be coated and said flow passage and said substrate are relatively displaced so that the coating is formed pregressively, on successive portions along said face.

5. A process according to claim 4, characterised in that said relative displacement occurs in a direction parallel with the direction in which the gas flows along said flow passage.

6. A process according to claim 5, characterised in that said face is the top face of a ribbon of glass which is in continuous movement at a speed of at least 2 metres per minute, parallel with its longitudinal axis and in the direction of said gas flow.

7. A process according to claim 6, characterised in that the length of said flow passage (i.e. its dimension measured in the direction of gas flow therethrough) is not more than 2.0 metres.

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ing is in the form of a chimney extending		<b>t</b> ;	i	s no
upwardly away from said face.			1	10 c:
19. A process according to any preceding				27
claim characterised in that said exhaust duct-			_	22 :
ing comprises a plurality of separate passage-	70	į	-	eed:
wave distributed in side by side relationship				disp
across substantially the whole width of the				said indu
are flow nath through said flow passage.				pass
20 A provess according to claim 19, charac-	75		10	2:
regised in that the exhaust of gas via different	15	-	10	22 I
exhaust ducting passageways is separately				ing
controlled.		•		disp
21. A process according to any preceding			1	into
claim, characterised in that said substrate is	80	•	15	dis <sub>F</sub>
a ribbon of glass formed by the float process and said flow passage is located downstream				
of the exit end of said tank and at a zone		•		.22
where the glass has a temperature in the	:			ing
range 100° to 650°C.				dis
22. Apparatus suitable for use in forming	85		20	saic
a metal or metal compound coating on a face	:			less
of a glass substrate by contacting such face	2			500
while it is at elevated temperature with a	a			cha
gaseous medium consisting of or containing a	3		25	COL
substance or substances in gaseous phase	, )		25	dis
which substance(s) undergo(es) chemical re-	•			llo.
action or decomposition to form said meta	11			to
or metal connecund on said face, said appara	1-			les
tus comprising means for supporting said	u		30	
substrate, means for heating such substrate	-, -		•	30
means for feeding gaseous medium into	d			co
space to which such face is exposed, and means for exhausting unused medium from	m			sti
such space, characterised in that the appara	a-			ale.
tus includes a shroud which is mounted in	a 100		35	to
position such that it defines with the sub	b-			2-
strate face to be coated a shallow flow passage	c,			27 <b>d</b> u
in that said feeding means is arranged in	or	:		in
discharging gaseous medium into such no	· W		. 40	_
naceage at one end thereof, and in that d	110	:	• •	ch ch
opposite end of said shallow now passay	ge			sl
leads into exhaust ducting via which residu	iai			b
medium can be drawn away from such	ch	,		
nactage	22, 110	•		
23 Apparatus according to claim 4		•		
t characterised in that the spacing of sa	na Di	:	-	
s shroud from said substrate supporting mea	102 1112			
e is such that when a substrate is in positi	VIA	~		
n for coating, the height of the shallow flor	at 115			
passage, measured nermally to said face, is				
no point in excess of 40 mm.  24. Apparatus according to claim 22 or 3	23.			
	ers			
1				
or towards said opposite end thereof.  A population according to any of claim	ims 120			

25. Apparatus according to any of claims 120

22 to 24, characterised in that means is pro-

vided for displacing a substrate, while sup-

ported by said substrate supporting means,

relative to said shroud and in the same direc-

tion as that in which gas flows along said

characterised in that the length of said shallow

flow passage (i.e. its dimension measured in

26. Apparatus according to claim 25,

the direction in which gas flows therethrough) 130

shallow flow passage.

8. A process according to claim 7, characterised in that the length of said flow passage (i.e. its dimension measured in the direction of gas flow therethrough) is not less than 10 cm.

9. A process according to any preceding claim, characterised in that a stream of oxygen or oxygen-containing gas and a separate stream of a vapourised metal compound with which oxygen reacts to form a metal oxide coating on said face feed continuously into said flow passage.

10. A process according to claim 9, characterised in that said gaseous medium contains a vapourised tin compound and a tin oxide

coating is formed on said face.

11. A process according to claim 9 or 10, characterised in that a gascous medium consisting of or containing a said vapourised metal compound is continuously discharged into said flow passage and induces a flow of air into and along such passage.

12. A process according to any of claims 9 to 11, wherein the gaseous medium enter-25 ing said flow passage comprises a layer of vapourised metal compound and a layer of oxygen-containing gas which is introduced between said layer of vapourised metal com-

pound and said face.

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13. A process according to any of claims 9 to 12, wherein the gaseous medium entering said flow passage comprises an upper layer of exygen-containing gas and a layer of vapourised metal compound which flows beneath such upper layer.

14. A process according to any preceding claim, characterised in that the composition of said medium and the temperature conditions to which it is exposed are such that said coating forms on said face at a rate of at

least 700 A per second.

15. A process according to any preceding claim, applied for coating a continuous ribbon of glass which is in movement parallel with its longitudinal axis and in the same direction as the direction of gas flow along said flow passage, characterised in that the gaseous medium flowing along said flow passage derives at least in part from a gas stream which enters said passage from a path which is at 45° or less to said face.

16. A process according to claim 15, characterised in that the gaseous medium flowing along said flow passage derives from two or more gas feed streams which enter said passage from paths whose average angle to

said face is 45° or less.

17. A process according to claim 15 or 16, characterised in that the gaseous medium flowing along said flow passage derives from gas feed streams of different compositions which enter said passage from paths which are at an angle of 20-35° to each other.

18. A process according to any preceding claim, characterised in that said exhaust duct-

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is not more than 2.0 metres and not less than

27. Apparatus according to any of claims 22 t 26, characterised in that said gas feeding means comprise at least one conduit disposed for discharging gaseous medium into said shallow flow passage and consequently inducing a flow of ambient air into said passage.

28. Apparatus according to any of claims 22 to 27, characterised in that said gas feeding means comprises at least two conduits disposed for discharging streams of gases into said shallow flow passage as flow layers

disposed one above the other.

29 Apparatus according to any of claims 22 to 28, characterised in that said gas feeding means comprises at least one conduit disposed for discharging a stream of gas into said shallow flow passage at an inclination of less than 45° to the substrate face to be coated.

30. Apparatus according to claim 29, characterised in that said gas feeding means comprises two or more conduits disposed for discharging streams of gas into said shallow flow passage along paths whose average angle to the substrate face to be coated is 45° or less.

31. Apparatus according to claim 29 or 30, characterised in that the gas feeding means comprises conduits disposed for discharging streams of gas into said shallow flow passage along paths which are at an angle of 20-35° to each other.

32. Apparatus according to any of claims 22 to 31, characterised in that said exhaust ducting is in the form of a chimney extending upwardly away from said face.

33. Apparatus according to claim 32, characterised in that the rear of said chimney slopes upwardly and rearwardly from the bottom thereof relative to the chimney front.

34. Apparatus according to claim 33, characterised in that the exhaust ducting comprises a plurality of separate exhaust passageways distributed in side by side relationship across substantially the whole width of the gas flow path through said shallow flow

35. Apparatus according to claim 34, characterised in that means is provided for independently controlling the exhaust of gases through said separate exhaust passage-

ways. 36. Apparatus according to any of claims 22 to 35, characterised in that said substrate supporting means is adapted to support a ribbon of glass having a width of at least 2 metres and moving parallel with its longitudinal axis, and in that the corresponding dimension i.e. the widthwise dimension of said shallow flow passage is at least 1.8 metres.

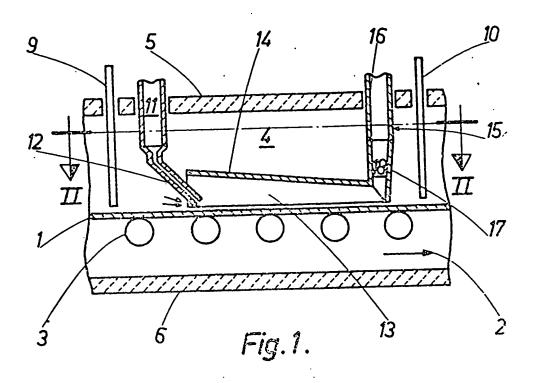
37. Apparatus according to any of claims 22 to 36, characterised in that it is disposed downstream of a float tank for use in the manufacture of a ribbon of glass by the float process, for coating the upper face of a said ribbon where the glass has a temperature in the range 100° to 650°C.

38. A process of forming a metal or metal compound coating on a face of a glass substrate, as claimed in claim 1 and substantially according to any of the Examples herein.

39. Apparatus suitable for use in forming a metal or metal compound coating on a face of a glass substrate, as claimed in claim 22 and substantially as herein described with reference to the accompanying drawings.

> HYDE, HEIDE & O'DONNELL, Chartered Patent Agents, 47, Victoria Street, London, SW1H 0ES. Agents for the Applicants.

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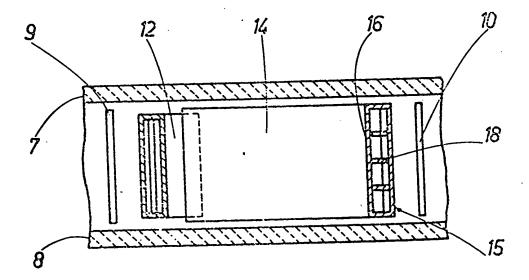
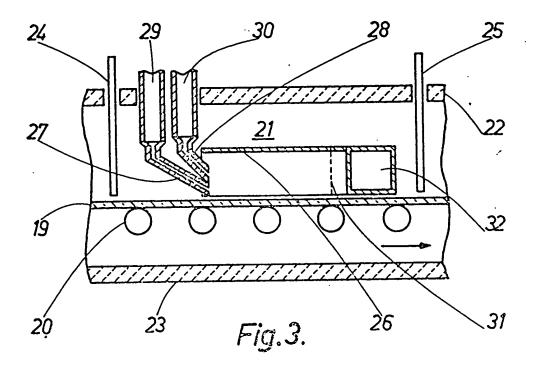


Fig.2.

1 524 326 COMPLETE SPECIFICATION
2 SHEETS This drawing is a reproduction of the Original on a reduced scale.
SHEET 2



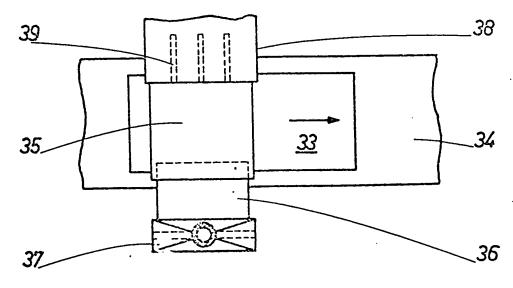


Fig.4.